

WE CLAIM:

1. A process for producing an image comprising the steps of:

- 5 (a) applying an opaque coating composition to the surface of a substrate wherein the surface is selected from the group consisting of light-emitting surfaces, reflective surfaces, glossy surfaces, and luminescent surfaces; and
- (b) contacting the coated substrate with a recording liquid, wherein the opaque coating composition becomes transparent upon printing.

10 2. The process of claim 1, wherein the image is a metallic-looking image.

3. The process of claim 1, wherein the opaque coating composition comprises a polyacid and a polybase.

15 4. The process of claim 3, wherein the polyacid contains two or more carboxylic, sulfonic and/or phosphonic acid groups and the polybase contains two or more primary, secondary or tertiary amine groups.

5. The process of claim 3, wherein the polyacid and polybase are monomeric.

20 6. The process of claim 1, wherein step (a) is repeated at least once, producing a multilayer coating on the substrate.

25 7. The process of claim 4, wherein at least two different opaque coating compositions are used in the repeated application steps (a).

8. The process of claim 5, wherein the monomeric polyacid has the structural formula (I)



5 wherein:

R is selected from the group consisting of alkyl, alkenyl, aryl of 1 to 3 rings which may be fused or linked, and 5- and 6-membered heterocyclic rings having from 1 to 3 heteroatoms selected from N, S and O;

L is an alkylene or alkenylene chain containing 1 to 8 carbon atoms;

10 x is 0 or 1;

y is an integer in the range of 2 to 10 inclusive; and

z is 1, 2 or 3,

with the provisos that (a) if w is 0 and x is 0, then y is 2 and z is 2, and (b) if z is 2 or 3, the distinct R groups are covalently linked to each other, and

15 the monomeric polybase has the structural formula (II)



20 wherein R¹ and R² are hydrogen, alkyl, alkoxy, or hydroxyl-substituted alkoxy, and R, L, x, y and z are as defined with respect to the monomeric polyacid.

9. The process of claim 8, wherein the monomeric polyacid is selected from the group consisting of oxalic acid, maleic acid, succinic acid, methylsuccinic acid, malonic acid, adipic acid, glutaric acid, fumaric acid, dihydroxyfumaric acid, malic acid, mesaconic acid, itaconic acid, phthalic acid, isophthalic acid, terephthalic acid, 1,2-, 1,3- and 1,4-cyclohexane dicarboxylic acids, 1,2,3-cyclohexane tricarboxylic acid, 1,2,4-cyclohexane tricarboxylic acid, 1,3,5-cyclohexane tricarboxylic acid, 1,2- and 1,3-cyclopentane dicarboxylic acids, citric acid, tartaric acid, dihydroxyterephthalic acid, 1,2,3-, 1,2,4- and 1,2,5-benzene tricarboxylic acids, tricarballic acid, 1,2,4,5-benzene tetracarboxylic acid, norbornene tetracarboxylic acid,

3,3',4,4'-benzophenone tetracarboxylic acid, 1,2,3,4,5,6-benzene hexacarboxylic acid, aspartic acid, glutamic acid, and combinations thereof.

10. The process of claim 8, wherein the monomeric polybase is selected from the group
5 consisting of ethylenediamine, 1,2-propane diamine, 1,3-propanediamine, 1,2,3-triaminopropane, *cis*-1,2-cyclohexanediamine, *trans*-1,2-cyclohexanediamine, 1,3-bis(aminomethyl)cyclohexane, *o*-, *m*- and *p*-phenylenediamine, tetramethyl *o*-, *m*- and *p*-phenylenediamine, hexamethylene-amine, hexamethylenetetraamine, diethylenetriamine, tetraethylenepentamine, pentaethylene-examine, pentamethyl diethylenetriamine, tris(2-
10 aminoethyl)amine, 1,1,4,7,10,10-hexamethyl triethylenetetraamine, tetramethyl-*p*-phenylenediamine, tetramethylethylenediamine, triethylenetetraamine, 4,4'-bipyridyl, and combinations thereof.

11. The process of claim 9, wherein the monomeric polybase is selected from the group
15 consisting of ethylenediamine, 1,2-propane diamine, 1,3-propanediamine, 1,2,3-triaminopropane, *cis*-1,2-cyclohexanediamine, *trans*-1,2-cyclohexanediamine, 1,3-bis(aminomethyl)cyclohexane, *o*-, *m*- and *p*-phenylenediamine, tetramethyl *o*-, *m*- and *p*-phenylenediamine, hexamethylene-amine, hexamethylenetetraamine, diethylenetriamine, tetraethylenepentamine, pentaethylene-examine, pentamethyl diethylenetriamine, tris(2-
20 aminoethyl)amine, 1,1,4,7,10,10-hexamethyl triethylenetetraamine, tetramethyl-*p*-phenylenediamine, tetramethylethylenediamine, triethylenetetraamine, 4,4'-bipyridyl, and combinations thereof.

12. The process of claim 3, wherein the polyacid and polybase are polymeric.

13. The process of claim 12, wherein the polymeric polyacid is a carboxylic acid-containing polymer and the polymeric polybase comprises a nitrogenous polymer.

14. The process of claim 13, wherein the polymeric polyacid is selected from the group consisting of poly(acrylic acid), poly(acrylonitrile-acrylic acid), poly(styrene-acrylic acid), poly(butadiene-acrylonitrile acrylic acid), poly(butylacrylate-acrylic acid), poly(ethyl acrylate-acrylic acid), poly(ethylene-propylene-acrylic acid), poly(propylene-acrylic acid), alginic acid, phytic acid, and combinations thereof, and the polymeric polybase is selected from the group consisting of polyethyleneimine, polyvinylpyridine, polyallylamine (including N-alkylated and N,N-dialkylated polyallylamines), polyvinylaziridine, polyimidazole, polylysine, chitosan, poly(amino and alkylated amino)ethylenes, ethoxylated polyethyleneimine, propoxylated polyethyleneimine, and combinations thereof.

15. The process of claim 3, wherein the polyacid is monomeric and the polybase is polymeric.

16. The process of claim 15, wherein the monomeric polyacid has the structural formula

(I)

(I)



wherein:

R is selected from the group consisting of alkyl, alkenyl, aryl of 1 to 3 rings which may be fused or linked, and 5- and 6-membered heterocyclic rings having from 1 to 3 heteroatoms selected from N, S and O;

L is an alkylene or alkenylene chain containing 1 to 8 carbon atoms;

x is 0 or 1;

y is an integer in the range of 2 to 10 inclusive; and

z is 1, 2 or 3,

with the provisos that (a) if w is 0 and x is 0, then y is 2 and z is 2, and (b) if z is 2 or 3, the distinct R groups are covalently linked to each other, and

the polymeric polybase comprises a nitrogenous polymer.

17. The process of claim 16, wherein the monomeric polyacid is selected from the group consisting of oxalic acid, maleic acid, succinic acid, methylsuccinic acid, malonic acid, adipic acid, glutaric acid, fumaric acid, dihydroxyfumaric acid, malic acid, mesaconic acid, itaconic acid, phthalic acid, isophthalic acid, terephthalic acid, 1,2-, 1,3- and 1,4-cyclohexane
5 dicarboxylic acids, 1,2,3-cyclohexane tricarboxylic acid, 1,2,4-cyclohexane tricarboxylic acid, 1,3,5-cyclohexane tricarboxylic acid, 1,2- and 1,3-cyclopentane dicarboxylic acids, citric acid, tartaric acid, dihydroxyterephthalic acid, 1,2,3-, 1,2,4- and 1,2,5-benzene tricarboxylic acids, tricarballylic acid, 1,2,4,5-benzene tetracarboxylic acid, norbornene tetracarboxylic acid, 3,3',4,4'-benzophenone tetracarboxylic acid, 1,2,3,4,5,6-benzene hexacarboxylic acid, aspartic
10 acid, glutamic acid, and combinations thereof, and the polymeric polybase is selected from the group consisting of polyethyleneimine, polyvinylpyridine, polyallylamine (including N-alkylated and N,N-dialkylated polyallylamines), polyvinylaziridine, polyimidazole, polylysine, chitosan, poly(amino and alkylated amino)ethylenes, ethoxylated polyethyleneimine, propoxylated polyethyleneimine, and combinations thereof.

18. The process of claim 3, wherein the polyacid is polymeric and the polybase is monomeric.

19. The process of claim 18, wherein the polymeric polyacid is a carboxylic acid-
20 containing polymer, and the monomeric polybase has the structural formula (II)



wherein:

25 R is selected from the group consisting of alkyl, alkenyl, aryl of 1 to 3 rings which may be fused or linked, and 5- and 6-membered heterocyclic rings having from 1 to 3 heteroatoms selected from N, S and O;

L is an alkylene or alkenylene chain containing 1 to 8 carbon atoms;

x is 0 or 1;

30 y is an integer in the range of 2 to 10 inclusive;

z is 1, 2 or 3; and

R¹ and R² are hydrogen, alkyl, alkoxy, or hydroxyl-substituted alkoxy,

with the provisos that (a) if w is 0 and x is 0, then y is 2 and z is 2, and (b) if z is 2 or 3, the distinct R groups are covalently linked to each other.

5
20. The process of claim 19, wherein the polymeric polyacid is selected from the group consisting of poly(acrylic acid), poly(acrylonitrile-acrylic acid), poly(styrene-acrylic acid), poly(butadiene-acrylonitrile acrylic acid), poly(butylacrylate-acrylic acid), poly(ethyl acrylate-acrylic acid), poly(ethylene-propylene-acrylic acid), poly(propylene-acrylic acid), alginic acid, phytic acid, and combinations thereof, and the monomeric polybase is selected from the group
10 consisting of ethylenediamine, 1,2-propane diamine, 1,3-propanediamine, 1,2,3-triaminopropane, *cis*-1,2-cyclohexanediamine, *trans*-1,2-cyclohexanediamine, 1,3-bis(aminomethyl)cyclohexane, *o*-, *m*- and *p*-phenylenediamine, tetramethyl *o*-, *m*- and *p*-phenylenediamine, hexamethylenediamine, hexamethylenetetraamine, diethylenetriamine,
15 tetraethylenepentamine, pentaethylenehexamine, pentamethyl diethylenetriamine, tris(2-aminoethyl)amine, 1,1,4,7,10,10-hexamethyl triethylenetetramine, tetramethyl-*p*-phenylenediamine, tetramethylethylenediamine, triethylenetetraamine, 4,4'-bipyridyl, and combinations thereof.

20 21. The process of claim 1, wherein the opaque coating composition is aqueous.

22. The process of claim 1, wherein the opaque coating composition includes a film-forming binder.

25 23. The process of claim 1, wherein the opaque coating composition further includes a colorant.

24. The process of claim 23, wherein the colorant is a pigment.

25. The process of claim 24, wherein the pigment is selected from the group consisting of silica, titanium dioxide, calcium silicate and calcium carbonate.

26. The process of claim 23, wherein the colorant is a dye.

27. The process of claim 1, wherein the opaque coating agent represents approximately 5 wt.% to approximately 95 wt.% of the image-enhancing composition, based upon total solids weight of the composition after drying.

28. The process of claim 1, wherein the film-forming binder represents approximately 1 wt.% to approximately 40 wt.% of the image-enhancing composition.

29. The process of claim 28, wherein the film-forming binder represents approximately 1 wt.% to approximately 50 wt.% of the image-enhancing composition.

30. The process of claim 29, wherein the film-forming binder represents approximately 1 wt.% to approximately 15 wt.% of the image-enhancing composition.

31. The process of claim 1, wherein the opaque coating composition further includes an optical brightener.

32. The process of claim 31, wherein the optical brightener represents approximately 0.01 wt.% to approximately 20 wt. % of the opaque coating composition.

33. The process of claim 1, wherein the opaque coating composition further includes a crosslinking agent.

34. The process of claim 33, wherein the crosslinking agent is ammonium zirconyl carbonate.

35. The process of claim 33, wherein the crosslinking agent is zirconium acetate.

36. The process of claim 1, wherein the surface of the substrate is reflective.

37. The process of claim 36, wherein the reflective surface is metallic.

38. The process of claim 1, wherein the substrate is a paper/foil laminate.

39. The process of claim 1, wherein the substrate is a metallized film.

40. The process of claim 1, wherein step (b) is performed using a writing instrument.

41. A substrate having a surface selected from the group consisting of glossy surfaces, reflective surfaces and luminescent surfaces, coated with an opaque coating composition that becomes transparent upon contact with an ink or solution.

42. The substrate of claims 41, wherein the opaque coating composition comprises a polyacid and a polybase.

43. The coated substrate of claim 41, wherein the substrate has a reflective surface.

44. The coated substrate of claim 43, wherein the reflective surface is metallic.

45. The coated substrate of claim 43, wherein the reflective surface is holographic.

46. The coated substrate of claim 41, wherein the substrate is comprised of a paper/foil laminate.

47. A process for producing an image comprising the steps of:

(a) printing a preselected image on a substrate surface selected from the group consisting of glossy surfaces, reflective surfaces, and luminescent surfaces;

(b) applying an opaque coating composition on the preselected image; and

-36-

(c) applying a recording liquid to the coated substrate,
wherein the opaque coating composition is such that it becomes increasingly
translucent or transparent upon printing.

5 48. The process of claim 47, wherein the opaque coating composition comprises a
polyacid and a polybase.

49. The process of claim 47, wherein the opaque coating composition further includes a
colorant.

10 50. The process of claim 47, wherein the substrate has a reflective surface.

51. The process of claim 48, wherein the reflective surface is metallic.

15 52. The process of claim 48, wherein the reflective surface is holographic.

53. The process of claim 47, wherein the substrate is comprised of a paper/foil laminate.

54. The process of claim 47, wherein the substrate is comprised of a metallized film.

20 55. The process of claim 47, wherein step(c) is carried out using a writing instrument.

56. A substrate having a surface selected from the group consisting of light emitting,
reflective surfaces and luminescent surfaces, having a preselected image or color scheme on the
25 surface additionally coated with an opaque coating composition that becomes increasingly
translucent or transparent upon contact with a recording liquid.

57. The substrate of claim 56, wherein the opaque coating composition comprises a
polyacid and a polybase.

-37-

58. The coated substrate of claim 56, wherein the substrate has a reflective surface.

59. The coated substrate of claim 56, wherein the reflective surface is metallic.

5 60. The coated substrate of claim 56, wherein the reflective surface is holographic.

61. The treated substrate of claim 56, wherein the substrate is comprised of a paper/foil laminate.

10 62. The treated substrate of claim 56, wherein the substrate is comprised of a metallized film.